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A SEARCH FOR NEW FUEL COMPONENTS IN
EXPLOSIVE MIXTURES WITH AMMONIUM NITRATE

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A SEARCH FOR NEW FUEL COMPONENTS
IN EXPLOSIVE MIXTURES WITH AMMONIUM NITRATE

4 SEP 1981

by

M.C. Neveu

ABSTRACT

A series of about 80 dye samples was tested by differential scanning calorimetry (DSC) for eutectic formation with ammonium nitrate and release of energy. Thirteen of these showed these desired characteristics. These were in the class of oxazines and dioxazines with ionic groups; and of ionic and non-ionic aminoanthraquinones. A discussion is given about the possibility of the non-ionic aminoanthraquinones to form eutectic mixtures with ammonium nitrate. A synthesis of 2,2',4,4',6,6'-hexanitro-3,3'-biphenol was carried out and its thermal properties as well as those of its potassium and ammonium salts were determined by differential scanning calorimetry. The significance of the use of dyes as fuels in fuel/oxidizer explosive systems and of the use of the Colour Index for the discovery of further intermolecularly reacting explosive systems is discussed.

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I. INTRODUCTION

It has been well demonstrated in recent and current research that chemical compounds can be chosen, or designed and synthesized, to produce nonideal explosives - particularly intermolecularly reacting ones - which have very attractive characteristics. The characteristics include performance, sensitivity, safety, low cost, industrial availability, strategic and tactical invulnerability, producibility, and mechanical properties.

1,2

This has been shown with three totally different systems:

(1) nitrate oxidizers and organic fuels (ethylenediamine dinitrate (EDD)/ ammonium nitrate (AN), for example; (2) systems in which a compound is specifically synthesized to form a eutectic around the ammonium moiety rather than the nitrate, and which behave almost ideally; (3) high-energy, high density inorganic fuel/oxidizer systems of hydrides and perchlorates.

The systems listed above are two-component intermolecularly reacting ones. One of the factors which governs their effectiveness as explosives is the particle size of the two components; the smaller the particle size, the larger the surface area available for each component to react with one another. This thrust towards smallest particle size leads logically to a search for systems whose components form solid solutions or eutectic mixtures where the particle size is essentially at the molecular size level. The effectively small particle size and high intimacy of the mixed compounds are expected to lead to enhanced performance of potential intermolecular explosives.

II. OBJECTIVES

One of the characteristics of a eutectic mixture is that of a lower melting point than either of its constituent components. The observation of a melting point depression in an approximately equimolar fuel/oxidizer mixture would indicate the formation of a eutectic. It was decided to screen a series of about 80 commercial dyes by Differential Scanning Calorimetry for eutectic mixture formation with ammonium nitrate as evidenced by an endothermic peak below the melting point of ammonium nitrate (169.6°C).

It was expected that certain functional groups in these dyes such as nitro, azo, phenolic, and amino, for example, might contribute to the explosive properties and/or facilitate the formation of eutectic mixtures with ammonium nitrate. Another attractive feature in the choice of dyes as potential fuel components in intermolecularly reacting explosives mixtures with ammonium nitrate is the high industrial production capacity of this country for the manufacture of a great variety of dyes, measured in terms of barrels and tons rather than grams in the case of specialty compounds prepared and synthesized on a laboratory bench scale. In addition, molecular structures, commercial sources, and methods of synthesis for all known dyes are tabulated in an extensive compilation entitled Colour Index.³ In this compilation, dyes are assigned a given Colour Index (C.I.) Number. In this arrangement, dyes with a specific major structural feature are enclosed within a given C.I. No. range (i.e. monoazo dyes 11000-19999; diazo dyes 20000-29999; xanthene dyes 45000-45999; anthraquinone dyes 58000-72999 etc.). Finding of explosive properties and eutectic mixture formation for a

particular dye would suggest that other dyes within the same C.I. No. classification system would show similar behavior. Thus, the classification system might be useful in the selection of other dyes with desirable properties. Indeed, because of molecular structure differences within a given C.I. No. range, differences in explosive characteristics among the members would be expected. A wide spectrum of explosive properties might be able to be formulated with fuels selected from a given C.I. No. range or from a variety of such ranges. The ultimate aim stemming from this concept would be the ability to "custom-tailor" an explosive with a specific explosive property profile by selection of an appropriate dye as organic fuel to be mixed with ammonium nitrate or other oxidizer. The immediate goal of this research project is the verification of the hypothesis that members of the same C.I. No. range will have similar behavioral characteristics and to generate initial data base upon which wide-spectrum formulation and "custom-tailoring" would eventually be founded.

Another phase of this research project was the preparation of a highly nitrated molecule, 2,2',4,4',6,6'-hexanitro-3,3'-biphenol and the investigation of its properties as well as those of its salts as potential explosives.

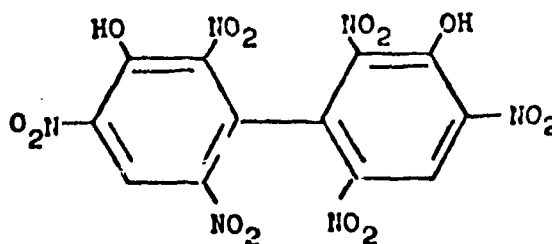


Figure I. 2,2',4,4',6,6'-hexanitro-3,3'-biphenol

III. FORMATION OF EUTECTIC MIXTURES BETWEEN DYES AND AMMONIUM NITRATE

Mixtures of dye and ammonium nitrate about 50% by weight in each component were studied with a Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1B. The DSC scans were carried out in two sweeps: the first from the temperature at which the DSC came under temperature control, 57°C, to 177°C - somewhat above the melting point of ammonium nitrate. This assured proper mixing of the two components. The second sweep was started, again, at 57°C and was carried on through any exotherm that followed.

Experiments which did not result in formation of eutectic mixtures usually showed identical DSC thermograms, specifically, two endotherms; one occurring at 127°C involving a phase transition for ammonium nitrate; the other at 170°C for the melting of ammonium nitrate. Experiments which did lead to eutectic mixture formation usually showed a disappearance or diminution of the 170°C melting of ammonium nitrate endotherm and the appearance of a new endotherm corresponding to the melting of the eutectic. This new endotherm was centered at 112°C (standard deviation 6.6°C) for the thirteen dyes showing eutectic mixture formation. The exotherm which followed was generally sharp and strong with a half-peak width between 2°C and 4°C. In several cases, the pen of the recorder went off-scale indicating the liberation of a great deal of energy. For the same set of dyes, the exotherm was centered at 235°C (standard deviation: 13.0°C).

Table I gives the DSC data for the dyes which formed eutectic mixtures. A copy of the Colour Index entry for all the dyes tested is given in Appendix A. A considerable number of samples tested have the same C.I. No. These entries include C.I. No.; commercial and alternative names; molecular structure (pi electrons of benzene rings have been omitted in this compendium); chemical and physical properties;

TABLE I Temperatures of endotherms and exotherms for eutectic mixtures

| Colour Index No. | (°C) | (°C) |
|------------------|--------------------------|-------------------------|
| | Temperature of endotherm | Temperature of exotherm |
| 51080 | 115 | 249 |
| 51120 | 129 | 222 |
| 51300 | 105 | 217 |
| 51310 | 105 | 230 |
| 56055 | 111 | 243 |
| 60710 | 109 | 227 |
| 61110 | 117 | 253 |
| 61500 | 109 | 241 |
| 61505 | 111 | 219 |
| 61515 | 113 | 249 |
| 61570 | 107 | 227 |
| 64500 | 117 | 242 |
| 65005 | 107 | 249 |

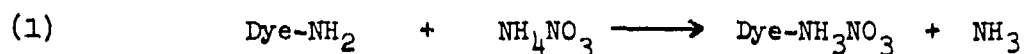
and lastly, literature and patent references. Lists of manufacturers for specific C.I. numbers can be obtained from other volumes of Colour Index.

Colour Index numbers 12010 through 26150, given in Appendix A, all azo or disazo dyes, gave negative results. It will be noted that these are all non-ionic. Conversion of these into salts (phenolate or ammonium) might result in eutectic formation, and possibility of taking advantage of the functional groups such as nitro and azo groups in their contribution to explosive properties.

Dyes from C.I. No. 51080 through 51319 all gave positive results

except for C.I. No. 51319. It might be noted that C.I. No. 51319 is non-ionic and the others in this grouping are ionic. These compounds are in the class of oxazines or dioxazines.

The series from C.I. No. 56055 through 65005 consisted of nine successful and four unsuccessful trials. Most of these are substituted anthraquinones with the exception of C.I. No. 56055 which has an analogous structure. The successful anthraquinones (or analogue) all have at least one amino group on a side benzene ring and many have two amino groups (somewhat remindful of the prototype eutectic forming fuel, ethylene diamine (as a double nitrate salt EDD, mentioned in the introductory portion of this report)). Two of these (C.I. No. 61570 and 65005) are already ionic. In the event that ionicity is necessary for eutectic mixture formation, it may be possible that the non-ionic dyes with amino groups reacted with excess ammonium nitrate to form the ammonium nitrate salt of the dye with the concomitant release of ammonia as follows:



Studies carried out at the High Explosives Research and Development Facility at Eglin AFB during a two-week visit at that facility between semesters of the 1980-1 academic year pointed to this conclusion. A program of converting the amino anthraquinones to their corresponding ammonium nitrate salts by neutralization with nitric acid and studying their eutectic forming ability with ammonium nitrate has been initiated in this laboratory.

IV. SYNTHESIS OF 2,2',4,4',6,6'-HEXANITRO-3,3'-BIPHENOL

The synthesis of the title hexanitrobiphenol was carried out by the nitration of 3,3'-biphenol. This latter compound is not commercially available and it was intended to prepare it by a fairly extended synthetic route described by Mascarelli and Visintin⁴. It was, however, discovered that one of the intermediate compounds in this synthetic route, namely 3,3'-dimethoxybiphenyl, was commercially available (Aldrich Chemical Co. Inc.; 940 W. St. Paul Ave.; Milwaukee, Wisconsin 53233). Consequently, the synthesis was considerably shortened to one involving the cleavage of 3,3'-dimethoxybiphenyl (A) to 3,3'-biphenol (B) followed by nitration to 2,2',4,4',6,6'-hexanitro-3,3'-biphenol (C) as shown in Figure II.

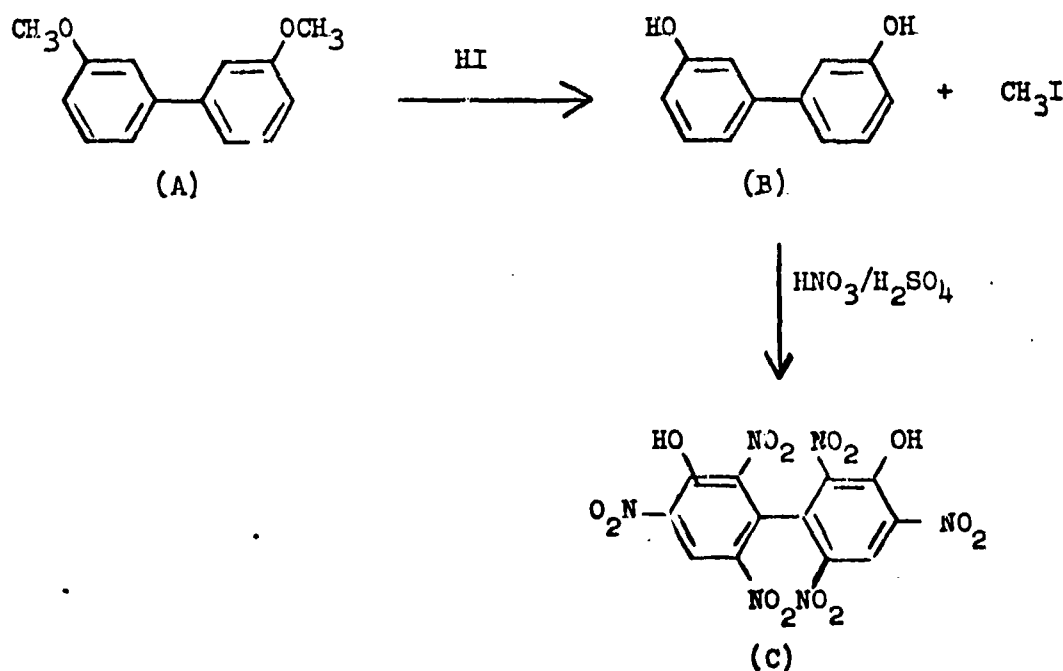


Figure II. Reaction scheme for the preparation of 2,2',4,4',6,6' - hexanitro - 3,3' - biphenol (C)

In a typical experiment involving the preparation of 3,3'-biphenol (B), 1.27 grams (5.93 millimoles) of 3,3'-dimethoxybiphenyl (A) was refluxed for 70 hours with 11.71 grams of a 47% by weight aqueous solution of hydrogen iodide (43.03 millimoles HI) in a distillation apparatus consisting of a 60 cm Vigreux column equipped with a distilling head capable of total reflux as well as take-off. Methyl iodide was removed periodically as it formed, and collected in the distilling head take-off tube. The reflux mixture was then cooled, and filtered through a sintered glass funnel of fine porosity to yield 0.79 grams (72% of theoretical yield) of 3,3'-biphenol. Recrystallization from benzene afforded white crystals melting at 125.4-126.4°C (literature value⁴: 123°C).

The nitration of the biphenol (B) prepared above was carried out in the following manner. A mixture consisting of 0.20 g (1.08 millimoles) of 3,3'-biphenol and 2.0 ml of 18 M sulfuric acid was heated with stirring at 100°C on a water bath for three hours. The mixture was then cooled to 80°C, and 2.0 ml of 15 M nitric acid (30.0 millimoles HNO₃) was then added to it. A vigorous evolution of brown fumes ensued and yellow crystals formed immediately. Heating was then stopped and the mixture was stirred overnight. The reaction mixture was filtered with a sintered glass funnel (fine); washed with benzene; and dried in a vacuum oven at 45°C for 75 hours to yield 0.32 grams of presumably hexanitrobiphenol (C) (64.4 % of theoretical yield) as yellow crystals.

Nuclear magnetic resonance (nmr) spectroscopic studies confirmed that the nitrated product above had structure (C). A multiplet centered at a delta value of 7.0 ppm in the nmr spectrum of 3,3'-biphenol (B) due to the hydrogen atoms on the aromatic rings disappeared in the spectrum of the nitrated product. A new peak, a singlet at a delta

value of 7.75 ppm appeared in the nmr spectrum of the nitrated product, indicating the presence of uncoupled hydrogen atoms at the 5 and 5' positions of the biphenyl system as in structure (C).

The DSC thermogram showed an exothermic peak at 275°C for the hexanitrated product (C). The potassium and ammonium salts of (C) were prepared by exact neutralization with potassium hydroxide and ammonium hydroxide. The potassium salt (orange) showed a melting endotherm at 108°C and an exotherm at 323°C. The ammonium salt (orange) gave an endotherm at 278°C and an exotherm at 303°C.

V. RECOMMENDATIONS

In view of the possibility that eutectic formation of non-ionic anthraquinones having amino groups may have been made possible by their conversion into ionic compounds by a "direct reaction" described by equation (1) on page 6, occurring while the DSC scan was being made, it would be of interest to convert these anthraquinones into nitrate salts by neutralization with nitric acid and isolate them. Their DSC thermograms could then be made and compared to the DSC thermograms of their corresponding non-ionic counterparts to obtain clues concerning the mechanism of their eutectic formation.

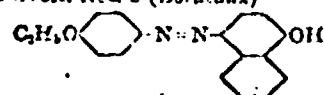
Another project that would be worth considering is the conversion of the non-ionic azo and disazo (yes into ionic compounds by the neutralization of the phenolic group with a suitable base to form sodium, potassium, or ammonium salts. Mixtures of these with ammonium nitrate could then be studied with DSC for eutectic formation with the possibility that this class of compounds with their attractive azo and nitro groups could be used in fuel/oxidizer eutectic mixtures.

It would also be of interest to make quantitative measurements on the exotherms obtained in this project. The exotherm could be scaled up to one having an accurately measurable area. With suitable calibration of the instrument with standards of accurately known heat capacities, the heat released during the exothermic stage of the DSC scan can be obtained from the measurement of the area of the exotherm. This quantitative data could then be used to compare the energy output of the systems studied in this work with each other and with other systems for which this data might be available or measurable.

Lastly, it might be well to construct phase diagrams for the systems studied in which melting points of a series of compositions of fuel and oxidizer are measured by DSC. This would verify the eutectic formation and would give the composition of the eutectic mixture. In addition, thermodynamic properties such as enthalpy, entropy, and free energy could be extracted from these.

APPENDIX A. Colour Index³ entries for dyes tested for eutectic mixture formation with ammonium nitrate

12010 C.I. Solvent Red 3 (Bordeaux)

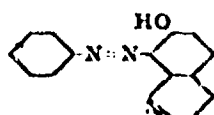


p-Phenoldioline → 1-Naphthol

Discoverers — O. N. Witt and A. Buntrock 1894
Witt & Buntrock, *Ber.* 27 (1894), 2360
FIAT 764 — Sudanbraun B

M.p. 168°C (bronze crystals)
Soluble in ethanol, acetone and benzene

12055 C.I. Solvent Yellow 14 (Reddish yellow)



Aniline → 2-Naphthol

Hauser & Breslow, *JACS*, 63 (1941), 419; *JSDC*, 57 (1941), 50.
Cross, *JSDC*, 61 (1945), 75

The following deal with metal complex derivatives —

Elkins & Hunter, *JCS*, (1935), 1598

Drew & Landquist, *Ibid.* (1938), 293

Drew & Fairbairn, *Ibid.* (1939), 824

Drew & Dunton, *Ibid.* (1940), 1065

M.p. 134°C

Soluble in ethanol (orange red), acetone and benzene

Insoluble in water

H₂SO₄ conc. — magenta red; on dilution — orange yellow ppt.

HCl conc. — red solution on warming, hydrochloride crystallises on cooling (dark green) but on separation and exposure loses hydrogen chloride

Discoverer — C. Liebermann 1883

FIAT 764 — Sudanorange R

Liebermann, *Ber.* 16 (1883), 2860

Zincke & Bindewald, *Ber.* 17 (1884), 3031

Marggery, *Gazz.* 14 (1884), 271

Zincke & Rathgen, *Ber.* 19 (1886), 2432

Denaro, *Gazz.* 15 (1885), 405

Zincke & Lawson, *Ber.* 20 (1887), 2973

Fischer & Wimmer, *Ibid.* 20 (1887), 1579

Weinberg, *Ibid.* 20 (1887), 3172

Jacobson, *Ibid.* 21 (1888), 415

Meldola & East, *JCS*, 53 (1888), 460

Meldola & Morgan, *Ibid.* 55 (1889), 603

Goldschmidt & Rossell, *Ber.* 23 (1890), 496

Goldschmidt & Brubacher, *Ibid.* 24 (1891), 2306

McPherson, *Ibid.* 28 (1895), 2418

Hantzsch, *Ibid.* 32 (1897), 3100

Mühlau & Strobach, *Ibid.* 33 (1900), 805

Mühlau & Kepel, *Ibid.* 33 (1900), 2873

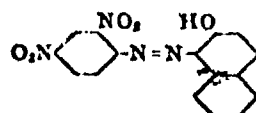
Blangey, *Helv. Chim. Acta*, 8 (1925), 750

Hodgson & Rosenberg, *JCS*, 1930, 2787

Bradley & Robinson, *Ibid.* 1934, 1484; cf. *JSDC*, 51 (1935), 37

Rowe & Dangerfield, *JSDC*, 52 (1936), 45

12075 C.I. Pigment Orange 5 (Bright reddish orange)



2,4-Dinitroaniline → 2-Naphthol

Discoverer — R. Lauch 1907

Agfa, *HP* 18736/08; *USP* 912138; *FP* 394754; *GP* 2172

(Fr. 9, 418)

BIOS 1661, 135

FIAT 764 — Permanentrot GG

Rowe & Levin, *JSDC*, 41 (1925), 355

Standard — BS 3599/4 C.I. Pigment Orange 5 (Dinitroaniline Red)

M.p. (from glacial acetic acid) 302°C small red crystals

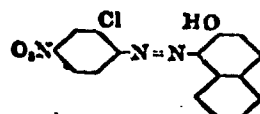
H₂SO₄ conc. — purple; on dilution — orange ppt.

HNO₃ — no change

NaOH — no change

4030

12085 C.I. Pigment Red 4 (Yellowish red, tint Reddish orange)



2-Chloro-4-nitroaniline → 2-Naphthol

Discoverers — W. Herzberg and O. Spengler 1907

Agfa, *USP* 865587; *FP* 368259; *GP* 180301 (Fr. 8, 704)

BIOS 1661, 137

FIAT 764 — Permanentrot R

Whitmore & Rivukas, *JACS*, 62 (1940), 1687

Standard — BS 3599/5 C.I. Pigment Red 4 (Chlorinated p-nitroaniline Red)

Slightly soluble in ethanol, acetone and benzene

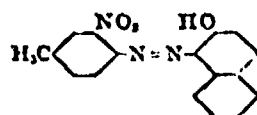
H₂SO₄ conc. — bluish magenta; on dilution — yellowish red ppt.

HNO₃ conc. — bright vermilion

NaOH dil. — no change

Alcoholic KOH — violet solution

12120 C.I. Pigment Red 3 (Yellowish red)



2-Nitro-p-toluidine → 2-Naphthol

Badische Co., BP 19100/05; FP 357853; GP ap. F20255 (Fr. 8, 725)

BIOS 1061, 49. BIOS 961, 114

FIAT 764 — Hansarot B

Shairaiishi, J. Chem. Ind. Tok. 22 (1919), 99

Rowe & Levin, JSDC, 37 (1921), 205

Everest & Wallwork, Ibid. 44 (1923), 102

Whitmore & Revukas, JACS, 62 (1940), 1687

Standards

BS 3599/1 C.I. Pigment Red 3 (Toluidine Red)

Holland NEN 1964 5271 Pigments. Test methods for Toluidine Red

M.p. 258°C

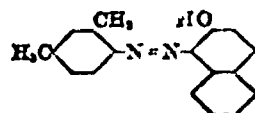
Slightly soluble in ethanol, acetone and benzene

H₂SO₄ conc. — deep reddish violet; on dilution — orange ppt.

HNO₃ conc. — dull vermillion

NaOH dil. — no change

12140 C.I. Solvent Orange 7 (Reddish orange)



2,4-Xylydine → 2-Naphthol

M.L.B., BP 5767/83; USP 306546; GP 29067 (Fr. 1, 549)

Bisulfite compound

FIAT 764 — Sudanorange RR

Mühlhäuser, Dingl. 264 (1887), 238

Rowe & Levin, JSDC, 40 (1924), 227

Cross, Ibid. 61 (1945), 75

M.p. (from glacial acetic acid) 166°C

Soluble in ethanol, acetone and benzene (reddish orange)

H₂SO₄ conc. — crimson; on dilution — crimson, then orange to reddish brown ppt.

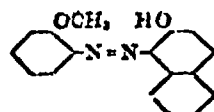
HNO₃ conc. — bright orange solution, becomes duller

NaOH 10% — insoluble (bleeds yellowish)

Alcoholic solution + HCl conc. — orange solution;

+ NaOH conc. — redder

12150 C.I. Solvent Red 1 (Yellowish red → Reddish orange)



o-Anisidine → 2-Naphthol

Discoverer — P. Griess 1899

Badische Co., USP 213563; GP 12451 (Fr. 1, 361)

FIAT 764 — Sudanrrot G

Vlies, JSDC, 30 (1914), 106

Rowe & Levin, Ibid. 40 (1924), 227

M.p. (from glacial acetic acid) 180°C

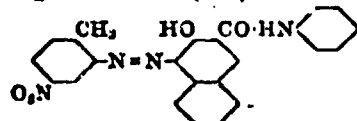
Soluble in ethanol (red; on boiling)

H₂SO₄ conc. — claret red; on dilution — dark red ppt.

Alcoholic solution + HCl — wine red;

+ NaOH — orange

12315 C.I. Pigment Red 22 (Red)

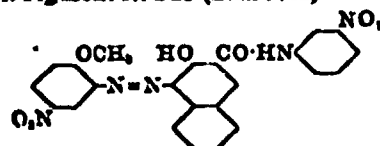


5-Nitro-o-toluidine → 3-Hydroxy-2-naphthanilide

Discoverers — A. Winther, A. Laska and A. Zitscher 1911

Patents as for C.I.12300

12355 C.I. Pigment Red 23 (Bluish red)

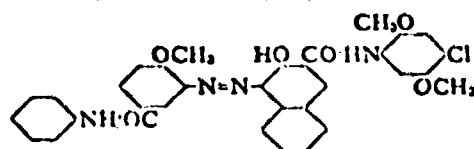


5-Nitro-o-anisidine → 3-Hydroxy-3'-nitro-2-naphthanilide

Discoverers — A. Winther, A. Laska and A. Zitscher 1911

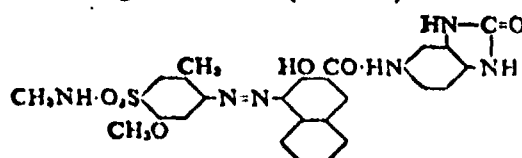
Patents as for C.I.12335

12485 C.I. Pigment Red 146 (Red)



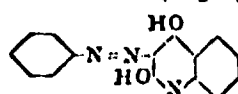
3-Amino-p-anisilide \rightarrow 4'-Chloro-3-hydroxy-2',5'-dimethoxy-2-naphthianilide

12516 C.I. Pigment Red 185 (Bluish red)



2-Methoxy-N',5'-dimethylsulfanilamide \rightarrow 3-Hydroxy-N-(2-oxo-5-benzimidazolyl)-2-naphthamide

12770 C.I. Disperse Yellow 4 (Bright greenish yellow)



Aniline \rightarrow 2,4-Quinolinediol

Discoverer — E. Fussenegger 1905

Badische Co., BP 11205/05; USP 806077; GP 165327 (Fr. 8, 718)

Brit. Dye Corp., BP 236037

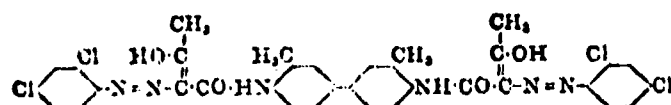
Rowe, RIC Lectures, 36

Green, Thorpe, 1, 41

For preparation of coupling component see — GP 117167 (Fr. 6, 1224)

Soluble in ethanol, acetone and toluene

20040 C.I. Pigment Yellow 16 (Greenish yellow)



2,4-Dichloroaniline (2 mol.) \rightarrow 4,4'-Bi-o-acetoacetotoluidide

Discoverers — A. Laska and A. Zitscher 1921

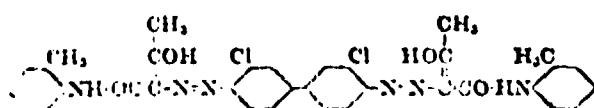
Griesheim-Elektron, BP 210217; GP 386054 (Fr. 14, 1006)

BIOS 1661, 144

FIAT 764 — Permanentgelb NGG (error for NCG)

FIAT 1313, 3, 473

21095 C.I. Pigment Yellow 14 (Yellow)



1,1'-Dichlorobenzidine \rightarrow o-Acetoacetotoluidide (2 mol.)

Griesheim-Elektron, GP 251479 (Fr. 11, 455)

BIOS 1661, 162

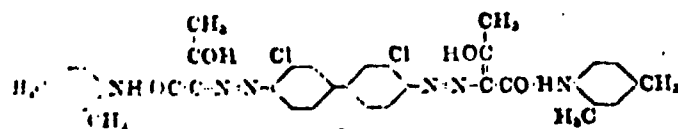
FIAT 764 — Vulcanechtgelb G

Insoluble in water

Very slightly soluble in toluene

H₂SO₄ conc. — bright reddish orange; on dilution — dirty greenish yellow ppt.

21100 C.I. Pigment Yellow 13 (Yellow)



1,1'-Dichlorobenzidine \rightarrow 2,4-Acetoacetoxylidide (2 mol.)

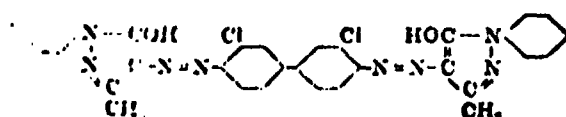
Griesheim-Elektron, GP 251479 (Fr. 11, 455)

BIOS 1661, 164

FIAT 764 — Vulcanechtgelb GR

FIAT 1313, 2, 280, 285

21110 C.I. Pigment Orange 13 (Reddish orange)



1,1'-Dichlorobenzidine \rightarrow 3-Methyl-1-phenyl-5-pyrazolone (2 mol.)

Discoverer — A. Laska 1910

Griesheim-Elektron, BP 1730/11; USP 1001286; FP 425429;

GP 236856 (Fr. 10, 937)

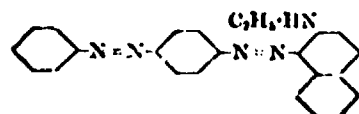
BIOS 1661, 122

FIAT 764 — Permanentorange G

H₂SO₄ conc. — bluish scarlet; on dilution — reddish orange ppt.

HNO₃ conc. — brownish scarlet

26050 C.I. Solvent Red 19 (Bright bluish red)

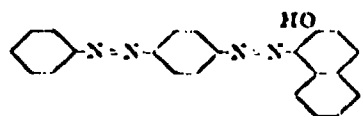


p-Phenyldiazoniline → *N*-Ethyl-2-naphthylamine

FIAT 764 — Sudanrot 7B

Soluble in ethanol (carmine)
Very soluble in acetone and benzene
H₂SO₄ conc. — brilliant greenish blue; on dilution — bluish violet to bordeaux

26100 C.I. Solvent Red 23 (Yellowish red)



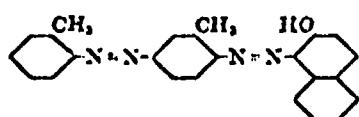
p-Phenyldiazoniline → 2-Naphthol

Note — Some commercial products are made from mixtures of *p*-phenyldiazoniline and its homologues and are e.g. composed of C.I. 26100 and C.I. 26105

Discoverer — F. Grüssler
Rumpff & Grüssler, BP 5003/79; FP 134802
Krügener, GP 16482 (Fr. 1, 443)
FIAT 764 — Sudan Red BK
Nietzki, Ber. 13 (1880), 800, 1838
Rowe & Levin, JSDC, 40 (1924), 226
Recrystallised from ethanol — brown plates with green metallic lustre, m.p. 195°C

Soluble in ethanol and acetone
Very soluble in benzene
H₂SO₄ conc. — bluish green; on dilution — blue solution, then red ppt.

26105 C.I. Solvent Red 24 (Red)

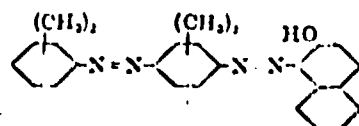


4-*p*-Tolylazo-*p*-toluidine → 2-Naphthol

FIAT 764 — Sudan Red BB
m.p. 184–185°C

Soluble in ethanol and acetone
Very soluble in benzene
H₂SO₄ conc. — bluish green; on dilution — red ppt.

26125 C.I. Solvent Red 27 (Bluish red)



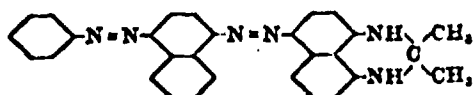
Xylyldiazoxylidine → 2-Naphthol

Note — For Sudan Red 5B (IG) the xylyldiazoxylidine was a mixed product obtained from technical mixed xylyldines (80%) and mixed toluidines (20%)

FIAT 764 — Sudanrot 5B
Evenson, J. Assoc. Off. Agric. Chem. 27 (1944), 572

Soluble in ethanol (yellowish red) and acetone
Very soluble in benzene
H₂SO₄ conc. — greenish blue; on dilution — bluish violet, ppt.

26150 C.I. Solvent Black 3 (Black)

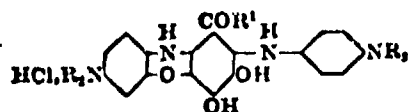


Aniline → 1-Naphthylamine → 2,3-Dihydro-2,2-dimethylperimidine

Badische Co., GP 278079 (Fr. 11, 1197)
FIAT 764 — Sudanschwarz BN, BT, 413

Soluble in ethanol, acetone and toluene
H₂SO₄ conc. — purplish black; on dilution — dull greenish blue
Ethanol solution + HCl conc. — bluish black;
+ NaOH conc. — dull blue

51050 C.I. Mordant Blue 35 (Greenish → Reddish navy)



R = CH₃ or C₂H₅; R' = NH₂ or OCH₃

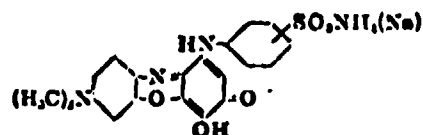
React the relevant gallocyanine with *N,N*-dimethyl (or diethyl)-*p*-phenylenediamine in presence of nitro (or *m*-dinitro)benzene and reduce to the leuco-compound

Discoverer — Loréann 1906
Durand & Huguenin, BP 21949/06; USP 844155; FP 376794;
GP 189940, 189941, (Fr. 9, 234, 235)
Ciba, BP 15751/15; USP 1227407
Grandmougin & Bodmer, J. prakt. Chem. 77 (1908), 508

Soluble in water (pale bluish green)
H₂SO₄ conc. — pale reddish brown (violet on addition of MnO₂);
on dilution — brownish
Aqueous solution + NaOH — oxidation to violet

51120 C.I. Mordant Blue 56 (Greenish blue)

Classical name Delphine Blue



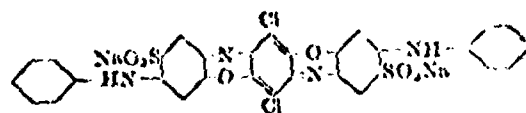
Heat aniline with the hydrochloride of Gallocyanine (C.I. 51030) and sulfonate; convert to the sodium salt

Note — The yield is improved by blowing air into the mixture while heating to prevent the formation of leuco-Gallocyanine, which does not condense with aniline

Discoverer — Hagenbach 1889
Kern & Sandoz, BP 569/90; FP 201463; GP 53942 (Fr. 2, 172)
Ciba, BP 15751/15; USP 1227407
Nietzki & Otto, Ber. 21 (1888), 1741
Grandmougin & Bodmer, Ber. 41 (1908), 604
Bodmer, Dissertation, Zürich, 1908, p. 74
Vlies, JSDC, 29 (1913), 321

Soluble in water (bluish violet)
H₂SO₄ conc. — reddish violet; on dilution — dark blue ppt.
Aqueous solution + NaOH — reddish ppt.

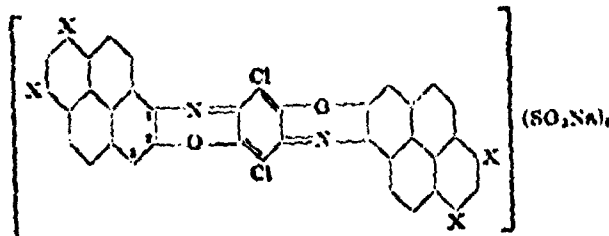
51300 C.I. Direct Blue 106 (Bright blue)



Condense 5-amino-2-anilinobenzenesulfonic acid with chloranil in water in presence of magnesium oxide as acid binding agent, cyclise the product to the dioxazine with oleum and isolate as disodium salt

Discoverers — Brunner, Greune, Thiele, and Thiess 1934
I.G., BP 448182; USP 2134505
BIOS 1482, 23. FIAT 1313, 3, 262
FIAT 764 — Siriuslichtblau FF2GL

51310 C.I. Direct Blue 109 (Greenish blue)

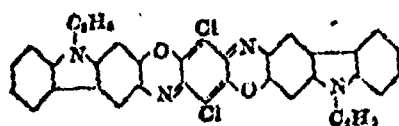


X = probable position of the SO₂Na groups

Condense 1-pyrenamine with chloranil, cyclise to dioxazine in boiling nitrobenzene, tetrasulfonate with oleum, and convert to tetrasodium salt

Discoverers — Kränzlein, Greune, and Schultheis 1932
I.G., BP 408456; USP 2016504; CP 606672 (Fr. 21, 1197)
BIOS 960, 79. FIAT 1313, 3, 261
FIAT 764 — Siriuslichtblau F3GL

51319 C.I. Pigment Violet 23 (Bluish violet)

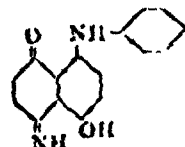


Condense 3-amino-9-ethylcarbazole with chloranil in trichlorobenzene

BP 387565 (IG)
CP 946560 (1952)
BIOS 960, 75
FIAT 1313, 3, 264
Jennison, J. D., Ph.D Thesis, Leeds 1963
Venkataraman 787

56055 C.I. Acid Black 47 (Bluish grey)

Sulfonated



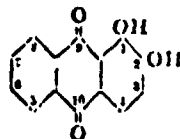
Condense 8-amino-5-hydroxy-1,4-naphthoquinone imine with aniline and sulfonate

BIOS 987, 141
FDX 885
FIAT 764 — Saecurizaringrau G
For preparation of the base see also Du Pont Co., USP 21353

55000 C.I. Mordant Red 11 (Aluminium in presence of Calcium → Bluish red)*

58000:1 C.I. Pigment Red 83 (metal complex)

Classical name Alizarin



- (a) Heat dibromoanthraquinone with potassium hydroxide
- (b) Heat 2-anthraquinonesulfonic acid (Na) with sodium hydroxide and a nitrate or chlorate
- (c) Heat anthraquinone with sodium hydroxide and sodium chlorate or nitrate (GP 186526)
- (d) Heat anthraquinone with sodium hydroxide and sodium nitrate in presence of sodium sulfite (GP 241806, 245987)
- (e) Heat *meso*-nitro derivatives of anthracene with sodium hydroxide in presence of oxidising agents, sodium sulfite and lime (GP 292247)
- (f) Treat 2-anthraquinonesulfonic acid in the presence of air with potassium hydroxide moistened with alcohol (GP 287270)
- (g) Alkali fuse 2-chloroanthraquinone in presence of sodium chlorate (USP 1744815)
- (h) Treat 2-methylanthraquinone with caustic alkali in presence of an oxidising agent (BP 293328)

Note — For information on naturally occurring Alizarin see C.I.75330

* Chromium-Dull bluish red; Iron-Dull purple

Grandinougis, *Compt. rend.* 173 (1921), 717, 1176
Tigerstedt, *Bull. Soc. ind. Mulhouse*, 90 (1924), 555
Scheurer, *Bull. Soc. ind. Mulhouse*, 91 (1925), 473
Tanaka, *Proc. Imp. Acad. Tokyo*, 3 (1927), 82
Philip, *J. I.C.S.*, 49 (1927), 473
Wahl, *Bull. Soc. chim.* 41 (1927) (IV), 1417
Schwenk, *Chem. Ztg.* 52 (1928), 45, 62
Minajev & Fedorov, *J. Chem. Ind. Russ.* 6 (1929), 535
Robertson, *J.C.S.*, (1930), 1136
Iljinski & Perelmann, *Chem. Zent.* 1 (1934), 1110; 1 (1937), 422, 433
Iljinski, *Chem. Zent.* 1 (1936), 1964
Karpuchin, *Chem. Zent.* 1 (1936), 2325
Georgievics, 231, 257
Bucherer, 336, 347
Barnett, 2, et al
Fierz-David, 524
Houben, 32, et al
Möhlau-Bucherer, 216
Mayer, 161
Fierz-David, Suppl. 79, 80
Thorpe, 1, 216
Venkataraman, 818

Soluble in acetone, alcohol (boiling), alkali, Cellosolve
Slightly soluble in benzene, carbon tetrachloride
Insoluble in alcohol (cold), Stoddard solvent
H₂SO₄ conc. — yellowish red; on dilution — reddish yellow ppt.
NaOH — violet

Discoverers — Robiquet and Colin (from Madder) 1826

C. Graebe and C. Liebermann (Prep. a) 1868

C. Graebe, C. Liebermann, and H. Caro (Prep. b) 1869

W. H. Perkin (Prep. b) 1869

Graebe & Liebermann, *BP* 3850/68; *USP* 95465

Graebe, Liebermann & Caro, *BP* 1936/69; *USP* 157534

W. H. Perkin, *BP* 1948/69, 3318/6

Dale & Schorlemmer, *BP* 216/70

M.I.B., *BP* 2649/72, 5444/74; *GP* 17627 (*Fr.* 1, 308), 81230 (*Fr.* 4, 334)

Auerbach & Gessert, *BP* 1269/74

Bayer, Weskott & Siller, *BP* 2071/74

Heinzerling & McGowan, *BP* 1712/75

Simpson, Brooke & Royle, *BP* 1851/76

Domier & Marzell, *BP* 2784/80

König, *BP* 2136/81

Brönnert, *BP* 759/82

Heffter, *GP* 36289 (*Fr.* 1, 308)

Leverkus & Söhner, *GP* 38454 (*Fr.* 1, 309)

Schaeffer, *BP* 20010/91, 21398/98

Badische Co., *BP* 7398/04, 20664/13; *FP* 344680; *GP* 186526 (*Fr.* 8, 237), 287270 (*Fr.* 12, 431)

Bayer Co., *BP* 19641/08, 2354/11, 24642/11, 11915/12; *USP* 1036880, 1036881; *FP* 395137, 435118; *Russ. P.* 23391; *GP* 241806, 245987, (*Fr.* 10, 594, 595), 249368, 251236, (*Fr.* 11, 586, 587)

Griesheim-Elektron, *BP* 16859/14; *USP* 1150152; *FP* 475141; *GP* 292247 (*Fr.* 12, 432)

Scottish Dyes, *BP* 174101, 246529, 293328; *USP* 1744815

BIOS 1484, 39; *FIAT* 764 — Alizarinrot B, G, R

Graebe & Liebermann, *Ber.* 1 (1868), 49, 104, 186; 2 (1869) 14, 332, 505; 3 (1870), 359, 636; *Ann. Suppl.* 7 (1870), 291 *Ann.* 160 (1871), 138

Strecker, *Z. Chem.* 4 (1868), 263

Perkin, *Ber.* 7 (1874), 972, 1106; 9 (1876), 281; *Ann.* 158 (1871), 319; *J. Soc. Arts*, 27 (1879), 527; *J.C.S.*, 23 (1870), 133; 29 (1876), 851; 37 (1880), 554; 69 (1896), 627

Auerbach, *Ber.* 4 (1871), 979

Liebermann, *Ber.* 4 (1871), 108; *Ann.* 183 (1876), 206

Böttger & Petersen, *Ber.* 4 (1871), 227; *Ann.* 160 (1871), 148

Baeyer & Caro, *Ber.* 8 (1875), 152

Liebermann & Troschke, *Ber.* 8 (1875), 379

Claus, *Ber.* 8 (1875), 530

Widmann, *Ber.* 9 (1876), 856

Baeyer, *Ber.* 9 (1876), 1232

Seuberlich, *Ber.* 10 (1877), 42

Schunck & Römer, *Ber.* 10 (1877), 175; 13 (1880), 42

Liebermann & Boeck, *Ber.* 11 (1878), 1613

von Perger, *J. prakt. Chem.* 18 (1878) (2), 118

Goppelsröder, *Dingl.* 228 (1878), 96; *J.S.D.C.*, 2 (1886), 63

Liebermann & Delmstedt, *Ber.* 12 (1879), 1293

Haushofer, *Jahresber.* (1882), 366

Levinstein, *J.S.C.I.*, 2 (1883), 213

Lukianoff, *Dingl.* 259 (1886), 97

Mullerus, *Chem. Ztg.* 17 (1893), 316, 374, 615

Erban and Specht, *Chem. Ztg.* 17 (1893), 542

Perkin, *J.S.D.C.*, 13 (1897), 81; *J.C.S.*, 75 (1899), 434, 445, 452; *J.S.C.I.*, 22 (1903), 605

Lagodzinski, *Ber.* 28 (1895), 1427; 36 (1903), 4020; *Ann.* 342 (1905), 88

Wacker, *J. prakt. Chem.* 54 (1896) (2), 88

Driessen, *Bull. Soc. ind. Mulhouse*, 63 (1902), 180

Liebermann & Hohenemser, *Ber.* 35 (1902), 1779

Ritter, *Chem. Ztg.* 27 (1903), 634

Persoz, *Bull. Soc. ind. Mulhouse*, 69 (1903), 193

Decker & Laube, *Ber.* 39 (1906), 112

Heller, *Z. angew. Chem.* 19 (1906), 669

Erban, *Z. Farb.-Ind.* 6 (1907), 7, 22, 50

Romann, *Bull. Soc. ind. Mulhouse*, 73 (1907), 174

Kempf, *J. prakt. Chem.* 78 (1908) (2), 257

Fehling, *Rev. gén. Mat. col.* (1909), 74

Battegay, *Bull. Soc. ind. Mulhouse*, 75 (1909), 348

Kornfeld, *Färberztg.* 21 (1910), 217

Freiberger, *Färberztg.* 23 (1912), 85, 109; *Bull. Soc. ind. Mulhouse*, 79 (1913), 651

Schmidt, *Bull. Soc. chim.* 15 (1914) (4), Suppl. I

Knecht & Hibbert, *J.S.D.C.*, 31 (1915), 241

Dimroth & Schultze, *Ann.* 411 (1916), 339; *Ber.* 54 (1921), 3028

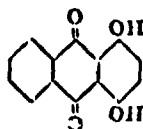
Leigh, *J.S.D.C.*, 32 (1916), 205

Diehl, *Färberztg.* 27 (1916), 134

Schull, *Ber.* 52 (1919), 565, 1142, 1829

Sunder, *Bull. Soc. ind. Mulhouse*, 87 (1921), 137; 90 (1924), 72; *Rev. gén. Mat. col.* 38 (1934), 129

58050 Smoke Dye (Orange)
58050:1 C.I. Pigment Violet 12 (Aluminium salt-Violet)
 Classical name Quinizarin



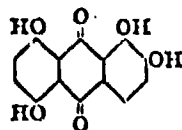
- (a) Treat anthraquinone with sulfuric acid in the presence of boric acid, boric acid and mercury, boric acid and nitrous acid or nitrous acid and mercury
- (b) Treat 1-hydroxyanthraquinone or 2-hydroxyanthraquinone with sulfuric acid in presence of boric and nitrous acids
- (c) Treat 1-hydroxy-4-nitroanthraquinone or 1,4-dichloroanthraquinone with sulfuric acid in the presence of boric acid
- (d) Condense phthalic anhydride and *p*-chlorophenol in presence of boric and sulfuric acids

Hahn, Wolf & Jäger, *Ber.* 57 (1924), 1394; *Z. anal. Chem.* 66 (1925), 106
 Brass & Ziegler, *Ber.* 58 (1925), 755
 Reynolds & Bigelow, *JACS*, 48 (1926), 420
 Green, *JCS* (1927), 2384
 Zahn & Ochwat, *Ann.* 462 (1928), 72
 Georgievics, 239
 Auerbach, 172, 250
 Fierz-David, 501
 Bucherer, 340, 348, 351, 354
 Barnett, 91, et al
 Houben, 32, et al
 Thorpe, 1, 220
 Venkatesaraman, 823

Soluble in ether
 H_2SO_4 , conc. — greenish yellow fluorescence

58500 C.I. Mordant Violet 26 (Chromium-Violet)

Classical name Quinalizarin



Oxidise alizarin or quinizarin with a large excess of fuming sulfuric acid and hydrolyse

Discoverer — F. Grimm 1873

Dye intermediate for colouring smokes Smoke Orange R (IG)
 Bayer Co., *BP* 973/94, 975/94, 12667/95, 27373/04, 27374/04, 1499/05; 28104/07, 12619/12; *USP* 1087412; *FP* 224740, 235896, 310329, 348927, 350957, 385358, 452244; *GP* 81245, 81960, 86630, (*Fr.* 4, 296, 274, 301), 125579, 135561, (*Fr.* 6, 335, 298), 161954, 162035, 162792, 163517 (*Fr.* 8, 252, 253, 253, 251), 203083 (*Fr.* 9, 681), 255031 (*Fr.* 11, 588)
 Badische Co., *BP* 7394/05; *USP* 754264; *FP* 338529; *GP* 153129 (*Fr.* 7, 182)

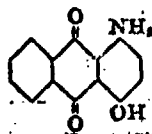
Scottish Dyes, *BP* 209694
 United Alk. Co., *BP* 245584
 Du Pont, *USP* 2003859
CIO XXVII-84, 62
 Grimm, *Ber.* 6 (1873), 506
 Kundt, *Ber.* 6 (1873), 511
 Baeyer & Caro, *Ber.* 7 (1874), 968; 8 (1875), 152
 Liebermann & Giesel, *Ber.* 8 (1875), 1646
 Liebermann, *Ann.* 183 (1876), 184; 212 (1882), 11; *Ber.* 10 (1877), 607; 11 (1878), 1610; 35 (1902), 1496
 Baeyer, *Ber.* 9 (1876), 1232
 Schunck & Römer, *Ber.* 10 (1877), 554, 1225
 Dralle, *Ber.* 17 (1884), 376
 Liebermann & von Kostanecki, *Ber.* 19 (1886), 2330
 Liebermann & Jellinek, *Ber.* 21 (1888), 1168
 Lagodzinski, *Ber.* 28 (1895), 117; 39 (1906), 1717
 Wacker, *J. prakt. Chem.* 54 (2) (1896), 90; *Ber.* 35 (1902), 3924
 Perkin, *JCS*, 75 (1899), 453
 Pleus, *Ber.* 35 (1902), 2993
 Georgievics, *Z. Farb.-Ind.* 1 (1902), 623; 4 (1905), 187; *Mhft. Chem.* 32 (1911), 329
 Dienel, *Ber.* 39 (1906), 926, 931
 Haslinger, *Ber.* 39 (1906), 3537
 Grandmougin, *J. prakt. Chem.* 76 (2) (1907), 139
 Pisovschi, *Ber.* 41 (1908), 1436
 Schmidt, *Bull. Soc. ind. Mulhouse*, 80 (1914), 431
 Meyer & Sander, *Ann.* 420 (1920), 113
 Ullmann & Conzetti, *Ber.* 53 (1921), 833
 Scholl, Dahl & Hansgig, *Ber.* 56 (1923), 2548

Discoverer — R. E. Schmidt 1890

Bayer Co., *BP* 8725/90, 17712/90, 4871/91; *USP* 446893; *FP* 206564; *GP* 60855, 63693, 67063, (*Fr.* 3, 193, 201, 203)
BIOS 1484, 27
 Liebermann & Wense, *Ber.* 20 (1887), 862
 Graebe, *Ber.* 23 (1890), 3739; *Ann.* 349 (1906), 205
 Schmidt, *J. prakt. Chem.* 43 (1891) (2), 237; *Bull. Soc. ind. Mulhouse*, 84 (1914), 428
 Hahn, Wolf & Jäger, *Ber.* 57 (1924), 1394
 Eegriwe, *Z. anal. Chem.* 76 (1929), 354
 Barnett, 257, 259, 260, 264
 Fierz-David, 542
 Houben, 326, 330, 366, 370

Soluble in alcohol
 H_2SO_4 , conc. — bluish violet; on dilution — dull red ppt.

60710 C.I. Disperse Red 15 (Bluish pink → Bluish red)



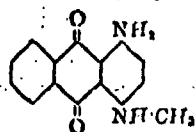
- (a) Partially acylate leuco-quinizarin with aqueous ammonia under pressure
- (b) Nitrate 1-hydroxyanthraquinone in sulfuric acid in presence of boric acid. Reduce the 1-hydroxy-4-nitroanthraquinone formed with aqueous sodium sulfide
- (c) Nitrate 1-methoxyanthraquinone, hydrolyse and reduce
- (d) Hydrolyse 1-benzamido-4-chloroanthraquinone

Discoverers — R. E. Schmidt and L. Gattermann 1876

Discoverers of use as dye for acetate — J. Baddiley and A. Shepherdson 1923
 Schmidt & Gattermann, *Ber.* 29 (1876), 2943
 Brit. Dye. Corp., *BP* 211720
I.G., *FP* 725054
BIOS 1484, 62; *CIO* XXVII-84, 62
CIO XXXII-58, App. 5; *FIAT* 1313, 2, 200
FIAT 764 — Cellitonechtrosa B, Rauchbordo BN
 Wacker, *Ber.* 35 (1902), 3293
 Ullmann & Conzetti, *Ber.* 53 (1920), 834
 Brass & Ziegler, *Ber.* 58 (1925), 763

Soluble in acetone, alcohol, benzene, linseed oil
 H_2SO_4 , conc. — dull yellow; on dilution — brown

61105 C.I. Disperse Violet 4 (Bright bluish violet)
C.I. Solvent Violet 12 (Bright bluish violet)

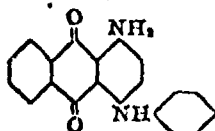


(a) Methylate leuco-1,4-diaminoanthraquinone with methanol in sulfuric acid in the presence of chlorine
(b) Treat leuco-quinizarin with ammonia and methylamine and oxidise

Discoverer — I.G.
BIOS 1484, 61; FIAT 1313, 2, 205
FIAT 764 — Cellitonechtviolett 5B
Thorpe, 1, 41

Soluble in acetone, benzene
Slightly soluble in alcohol
Insoluble in linseed oil
H₂SO₄ conc. — brown; on dilution — red

61110 C.I. Disperse Blue 19 (Bright reddish blue)
C.I. Solvent Blue 68 (Reddish blue)

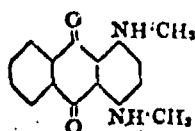


Condense 1-amino-4-hydroxyanthraquinone with aniline in the presence of boric acid

Discoverer — Bayer Co. 1900
Bayer Co., GP 125666 (Fr. 6, 370)
FDX 885 (PB 74722) — Setacyldirektblau RS
Mellor & Olpin, JSDC, 67 (1951), 621

Soluble in acetone, alcohol, benzene, Cellosolve
Slightly soluble in carbon tetrachloride
H₂O, conc. — dull bluish violet; on dilution — dull blue ppt.

61500 C.I. Disperse Blue 14 (Bright blue)

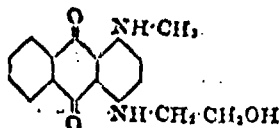


Treat quinizarin under pressure with aqueous methylamine and sodium hydrosulfite or zinc dust. Oxidise the leuco compound with nitrobenzene, or hot sulfuric acid

Discoverer — I.G. 1927
M.L.B., BP 15355/08
Brit. Celanese, BP 219349
Brit. Dye, Corp., BP 268891
BIOS 1484, 54; FIAT 1313, 2, 206
FIAT 764 — Cellitonechtblau B

Soluble in acetone, alcohol, glacial acetic acid, nitrobenzene, pyridine, toluene
H₂SO₄ conc. — reddish brown

61505 C.I. Disperse Blue 3 (Bright blue)



(a) Condense methylamine and ethanamine with quinizarin and leuco-quinizarin in isobutanol and oxidise
(b) Condense 1-bromo-4-methylaminoanthraquinone with ethanolamine in presence of copper acetate
Note — According to BIOS 987, 1,4-bis(methylamino)- and 1,4-bis(2-hydroxyethylamino)anthraquinone are also present

Discoverers — K. Köberle, R. Schweizer, C. Steigerwald, E. Runne, and L. Berlin 1933
I.G., BP 434906, 447037, 447090, 447107, 447103; USP 2051004;
GP 636834 (Fr. 23, 988), 722593
BIOS 987, 155; BIOS 1484, 57; FIAT 1313, 2, 206
FIAT 764 — Cellitonechtblau FFR

Soluble in acetone, alcohol, benzene, Cellosolve
Slightly soluble in carbon tetrachloride
Insoluble in Stoddard solvent
H₂SO₄ conc. — brown; on dilution — dull red

61515 C.I. Disperse Blue 24 (Bright blue)



Brominate 1-methylaminoanthraquinone and condense with aniline

Discoverer — Bayer Co. 1901
GP 159129 (Fr. 8, 323); GP 175069 (Fr. 8, 291)

Soluble in acetone, alcohol, benzene

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2. I. Akst (for Idos Corporation) "Nonideal Explosives Research at the High Explosives Research and Development Facility, Monthly Progress Report, August 1978, for ADTC/DLDE Eglin Air Force Base, Florida, Contract F08635-78-C-0215.
3. Colour Index, third edition, published by the Society of Dyers and Colourists, Yorkshire, England, 1975.
4. L. Mascarelli and B. Visintin, Gazz. chim. ital., vol. 62, pp. 358-368, 1932.